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Shimizu et al.

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(54) **FILM FORMING METHOD AND FILM FORMING APPARATUS**

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(30) **Foreign Application Priority Data**

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H01L 21/02 (2006.01)
C23C 16/40 (2006.01)
C23C 16/455 (2006.01)

(52) **U.S. Cl.**

CPC ***H01L 21/0228*** (2013.01); ***C23C 16/405*** (2013.01); ***C23C 16/45527*** (2013.01); ***C23C 16/45561*** (2013.01); ***H01L 21/02189*** (2013.01)

(58) **Field of Classification Search**

CPC C23C 16/405; C23C 16/45527; C23C 16/45561
USPC 427/248.1
See application file for complete search history.

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(57) **ABSTRACT**

A method of forming an oxide film on an object to be processed, includes: supplying a film-forming raw material gas into a processing chamber; performing at least one of exhausting the processing chamber and supplying a purge gas into the processing chamber to remove gas remaining in the processing chamber; supplying an oxidant gas into the processing chamber; and performing at least one of exhausting the processing chamber and supplying the purge gas into the processing chamber to remove gas remaining in the processing chamber, wherein supplying an oxidant gas includes: supplying a first oxidant gas into the processing chamber at a first concentration; and supplying a second oxidant gas into the processing chamber at a second concentration higher than the first concentration.

8 Claims, 6 Drawing Sheets

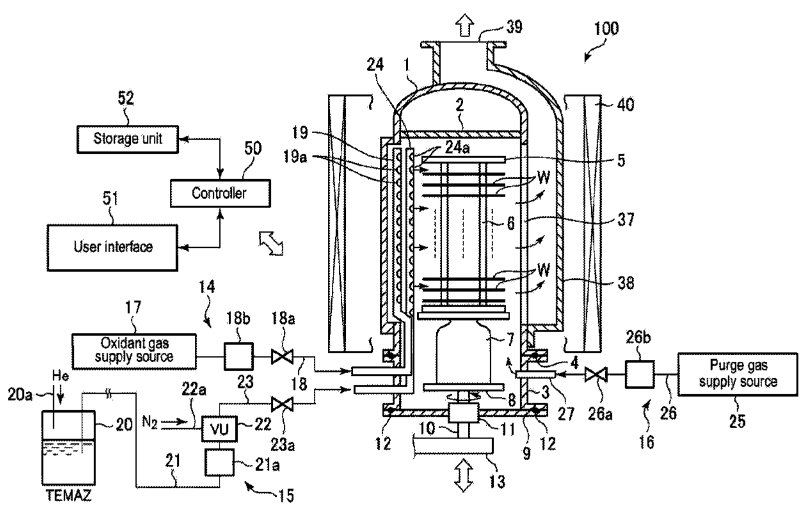


FIG. 1

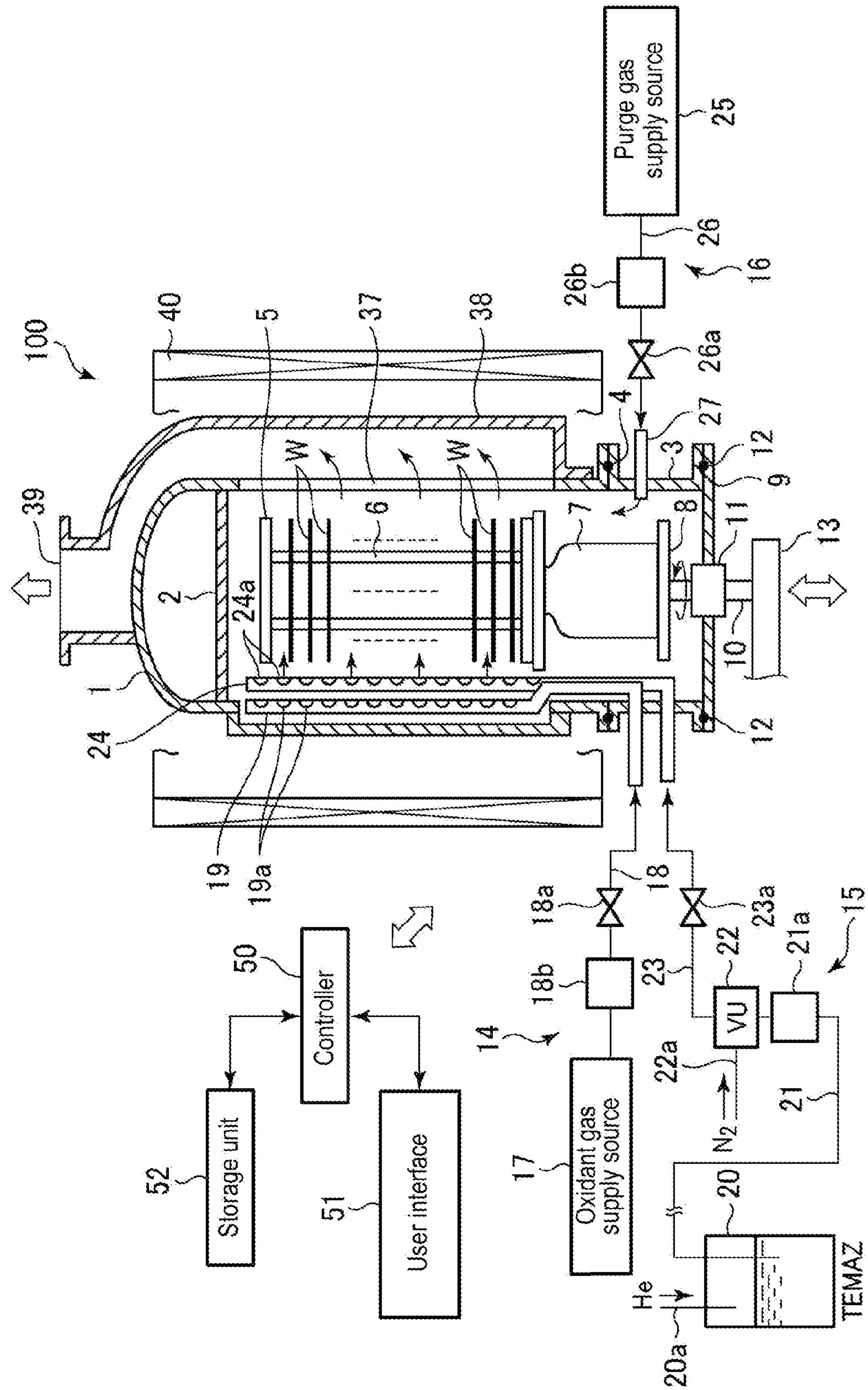

Purge gas supply source
Controller
Storage unit
User interface
Oxidant gas supply source
VU
N_2
He
TEMAZ
W
100
39
40
5
37
38
2
24a
6
7
8
1
24
19
19a
26
26b
26a
25
16
4
27
3
12
9
11
13
10
18
18a
18b
23
23a
22
21a
15
14
17
22a
21
20
20a
50
51
52

FIG. 2

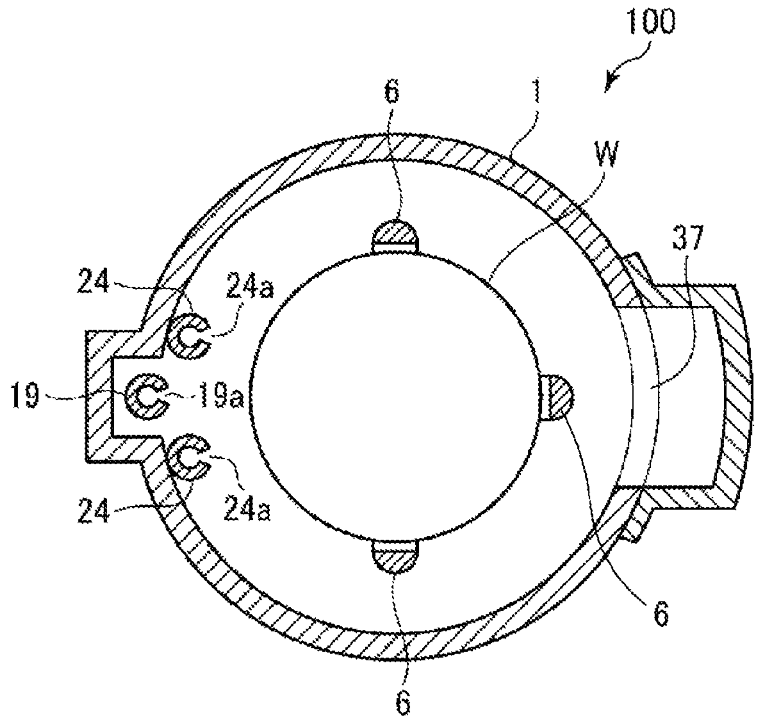


FIG. 3

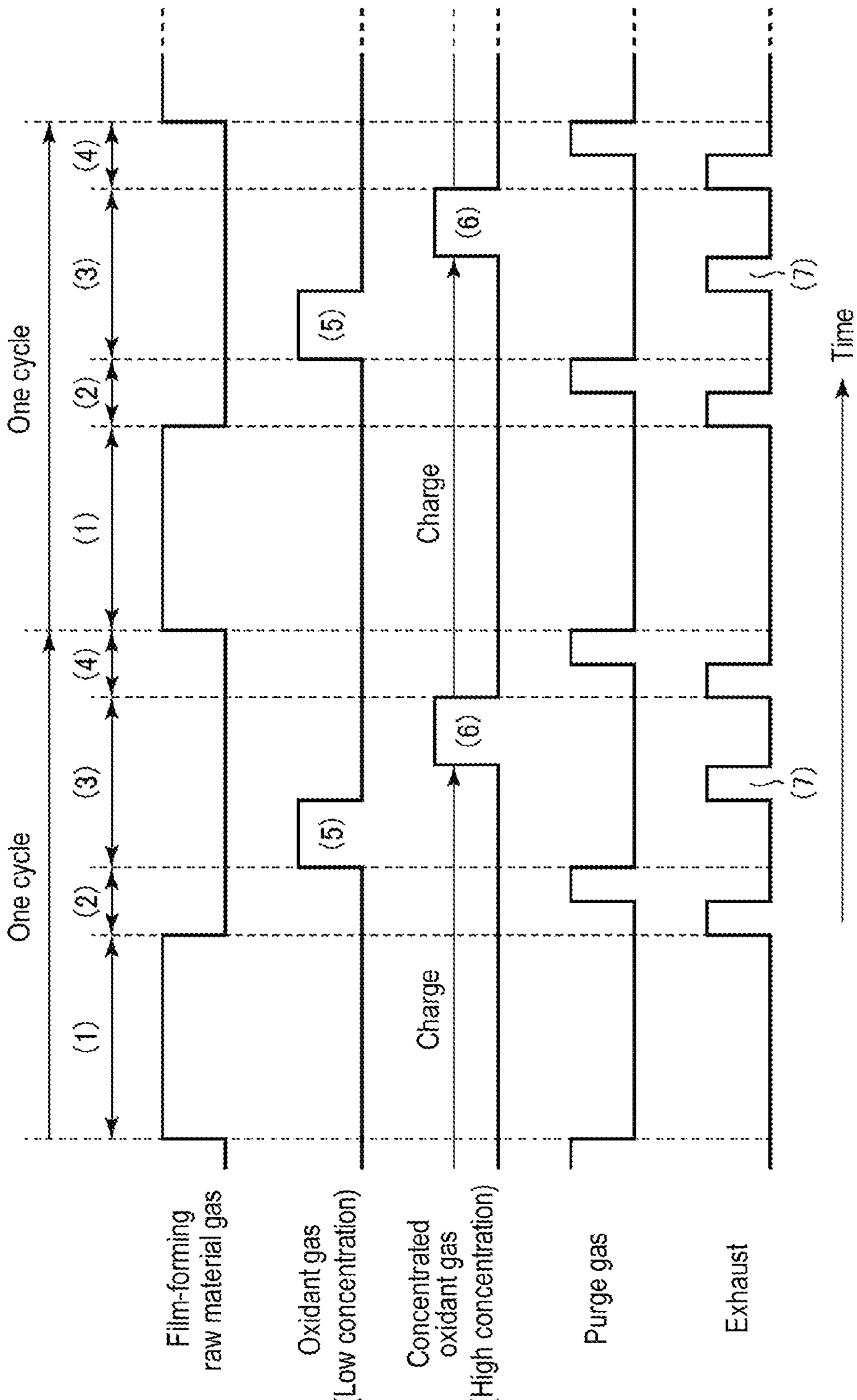

Film-forming raw material gas
Oxidant gas (Low concentration)
Concentrated oxidant gas (High concentration)
Purge gas
Exhaust
One cycle
One cycle
(1)
(2)
(3)
(4)
(5)
(6)
(7)
Charge
Charge
Time

FIG. 4A

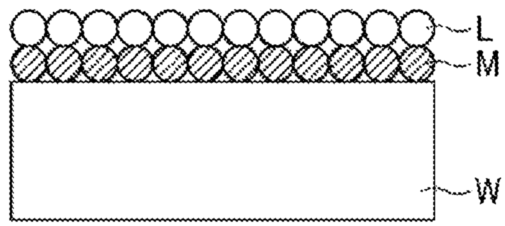


FIG. 4B

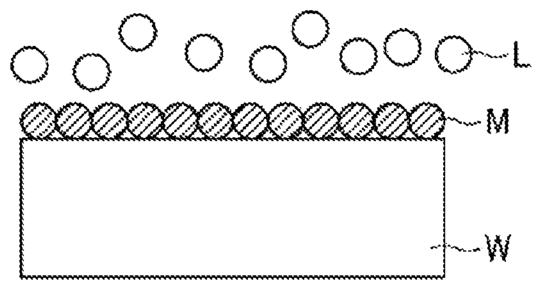


FIG. 4C

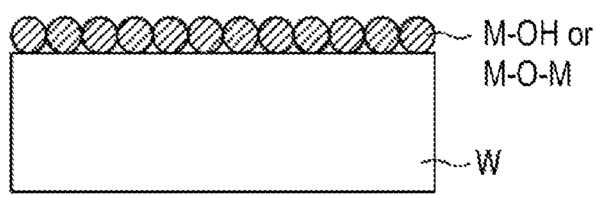
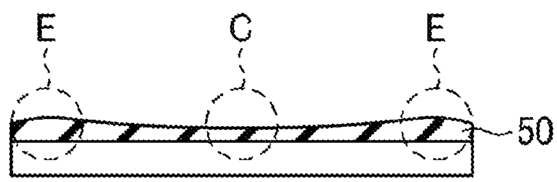


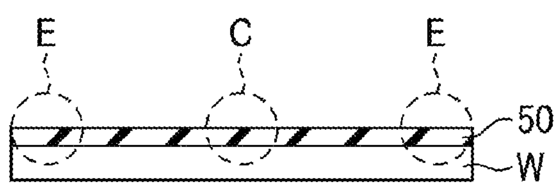
FIG. 4D

FIG. 5A



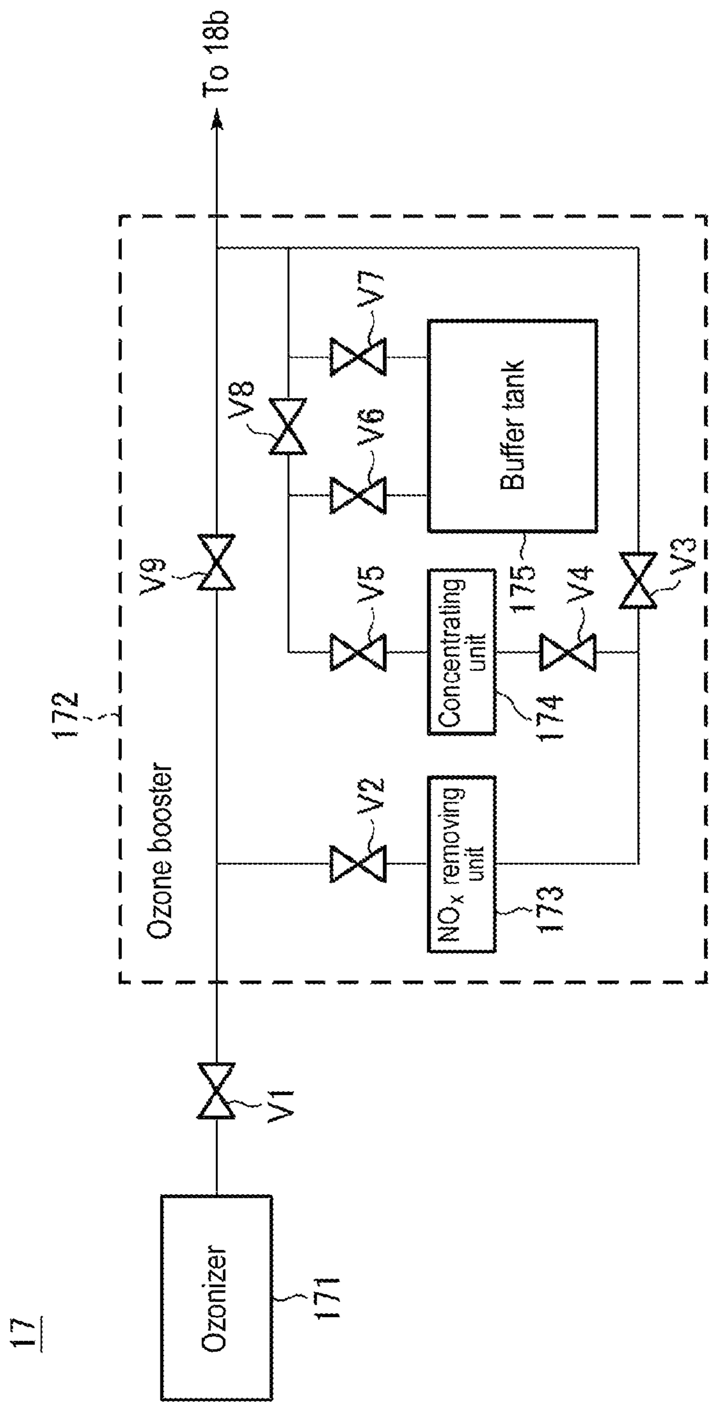
Comparative Example

FIG. 5B



Embodiment

FIG. 6


17
Ozonizer
171
V1
Ozone booster
172
V9
To 18b
V2
NO_x removing unit
173
V3
V4
Concentrating unit
174
V5
V6
V7
V8
Buffer tank
175

FILM FORMING METHOD AND FILM FORMING APPARATUS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of Japanese Patent Application No. 2013-073125, filed on Mar. 29, 2013, in the Japan Patent Office, the disclosure of which is incorporated herein in its entirety by reference.

TECHNICAL FIELD

The present disclosure relates to a film forming method and a film forming apparatus.

BACKGROUND

Recently, an increasing number of highly-integrated and high speed Large Scale Integrated (LSI) circuits is in demand. Thus, design rules of semiconductor elements constituting the LSI circuits are increasingly miniaturized. Such miniaturization requires further decreasing the thickness of a gate insulating film used in a CMOS device, which creates a need for the gate insulating film to be made of a material having high permittivity. In addition, there is a need to increase the number of capacitors used in Dynamic Random Access Memories (DRAMs) or the like. There is also a need to improve a permittivity of a dielectric film used in the capacitors. In addition, a flash memory is required to have a further improved reliability. As such, the gate insulating film formed between a control gate and a floating gate is required to have a high permittivity.

An oxide material such as a zirconium oxide (ZrO_2) film is being studied as a high-permittivity material which is adaptable to address the above requirements. The zirconium oxide film is formed by a chemical vapor deposition (CVD) (or a metal organic chemical vapor deposition (MOCVD)) using an organic metal material. In addition, as a method of forming the zirconium oxide film, there is proposed an ALD process which alternately supplies tetrakisethylmethylamino zirconium (TEMAZ) used as a raw material gas (precursor) and an O_3 gas used as an oxidant gas.

An in-plane uniformity of a metal oxide film such as the zirconium oxide film, which is obtained by the existing ALD process is 3 to 10%. Although the in-plane uniformity of the metal oxide film in the existing LSIs is sufficient with 3%, there is a need for an in-plane uniformity of less than 3% in consideration of miniaturization of future LSIs.

However, in the existing ALD process, the in-plane uniformity is hardly lower than 3%. Deterioration of the in-plane uniformity is drastically manifested when an oxidizing power of an O_3 gas is strengthened to make the metal oxide film denser. For example, assuming that a concentration of the O_3 gas is increased to strengthen the oxidizing power thereof, the O_3 gas having the increased concentration may oxidize ligands in addition to the precursor adsorbed onto a wafer.

When an organic metal is used as the precursor, the ligands become organic ligands such as CH_3 or C_2H_5. Oxidation of the organic ligands generates a H_2O or CO_x gas. In addition, if nitrogen is contained in the organic metal, a NO_x gas may be further generated.

In particular, the H_2O gas inactivates the O_3 gas. As such, a central portion of the wafer is hardly oxidized, thus causing the metal oxide film formed on the wafer to be thick at a periphery of the wafer and thin at the central portion thereof.

SUMMARY

Some embodiments of the present disclosure provide a method and apparatus which is capable of forming a metal oxide film having a dense and good in-plane uniformity even when a concentration of an oxidant gas used in oxidizing metal is increased to strengthen an oxidizing power thereof.

According to one embodiment of the present disclosure, there is provided a method of forming an oxide film on an object to be processed, includes: supplying a film-forming raw material gas into a processing chamber; performing at least one of exhausting the processing chamber and supplying a purge gas into the processing chamber to remove gas remaining in the processing chamber; supplying an oxidant gas into the processing chamber; and performing at least one of exhausting the processing chamber and supplying the purge gas into the processing chamber to remove gas remaining in the processing chamber, wherein supplying an oxidant gas includes: supplying a first oxidant gas into the processing chamber at a first concentration; and supplying a second oxidant gas into the processing chamber at a second concentration higher than the first concentration.

According to another embodiment of the present disclosure, there is provided a film forming apparatus, which includes: a processing chamber in which an oxide film is formed on each of a plurality of objects to be processed accommodated therein; a film-forming raw material gas source configured to supply a film-forming raw material gas into the processing chamber; an oxidant gas supply source configured to supply an oxidant gas into the processing chamber; a purge gas supply source configured to supply a purge gas into the processing chamber; an exhausting unit configured to exhaust the processing chamber; and a controller configured to control the film-forming raw material gas source, the oxidant gas supply source, the purge gas supply source and the exhausting unit to perform the aforementioned film forming method.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the present disclosure, and together with the general description given above and the detailed description of the embodiments given below, serve to explain the principles of the present disclosure.

FIG. **1** is a longitudinal sectional view showing an example of a film forming apparatus according to a first embodiment of the present disclosure, which is capable of performing a film forming method according to a second embodiment of the present disclosure.

FIG. **2** is a transverse cross sectional view of the film forming apparatus shown in FIG. **1**.

FIG. **3** is a timing chart showing an example of gas supply timings in the film forming method according to the second embodiment of the present disclosure.

FIGS. **4**A to **4**D are views schematically showing a state of an object to be processed in major processes of the example shown in FIG. **3**.

FIG. **5**A is a cross sectional view of a metal oxide film formed using a film forming method according to a comparative example.

FIG. 5B is a cross sectional view of a metal oxide film formed using the film forming method according to the second embodiment of the present disclosure.

FIG. 6 is a block diagram showing an example of a configuration of a oxidant gas supply source which is provided to perform the film forming method according to the second embodiment of the present disclosure.

DETAILED DESCRIPTION

Reference will now be made in detail to various embodiments, examples of which are illustrated in the accompanying drawings. In the following detailed description, numerous specific details are set forth in order to provide a thorough understanding of the present disclosure. However, it will be apparent to one of ordinary skill in the art that the present disclosure may be practiced without these specific details. In other instances, well-known methods, procedures, systems, and components have not been described in detail so as not to unnecessarily obscure aspects of the various embodiments. Throughout the drawings, the same elements are denoted by the same reference numerals.

(Film Forming Apparatus)

FIG. **1** is a longitudinal sectional view showing an example of a film forming apparatus **100** according to a first embodiment of the present disclosure, which is capable of performing a film forming method according to a second embodiment of the present disclosure. FIG. **2** is a transverse cross sectional view of the film forming apparatus **100** shown in FIG. **1**. A heating unit is omitted in FIG. **2**.

The film forming apparatus **100** includes a cylindrical-shaped processing chamber **1** having a ceiling, of which a lower end portion is opened. The entirety of the processing chamber **1** is formed of, e.g., quartz. A ceiling plate **2** of quartz is installed at the ceiling inside the processing chamber **1** such that the processing chamber **1** is sealed. Also, a manifold **3** which is formed of, e.g., stainless steel to have a cylindrical shape, is connected to a lower end opening portion of the processing chamber **1** through a seal member **4** such as an O-ring.

The manifold **3** supports a lower end portion of the processing chamber **1**. A wafer boat **5** of quartz, in which a plurality (e.g., 50 to 100) of semiconductor wafers (hereinafter, referred to as "wafers" simply) W are loaded as objects to be processed in multiple stages, is insertable into the processing chamber **1** through a lower portion of the manifold **3**. The wafer boat **5** includes three support pillars **6** (see FIG. **2**). Each of the plurality of wafers W is supported by grooves which are formed in each of the support pillars **6**.

The wafer boat **5** is placed on a table **8** through a heat insulating tube **7** of quartz. The table **8** is supported on a rotation axis **10** that passes through a cover part **9** of the stainless steel. The cover part **9** opens or closes a lower end opening portion of the manifold **3**.

A magnetic fluid seal **11** is installed at a through portion of the rotation axis **10**. The magnetic fluid seal **11** closely seals and rotatably supports the rotation axis **10**. Also, a seal member **12** such as an O-ring is installed between a peripheral portion of the cover part **9** and a lower end portion of the manifold **3**, thus maintaining sealability in the processing chamber **1**.

The rotation axis **10** is installed at a front end of an arm **13** that is supported by an ascending/descending mechanism such as a boat elevator. The rotation axis **10** ascends or descends the wafer boat **5** and the cover part **9** integratedly, and is inserted into or detached from the processing chamber **1**. In some embodiments, the table **8** may be installed to be fixed to the cover part **9** side such that the wafer W is treated without the rotation of the wafer boat **5**.

The film forming apparatus **100** further includes an oxidant gas supply mechanism **14** configured to supply an oxidant gas into the processing chamber **1**, a film-forming raw material gas supply mechanism **15** configured to supply a film-forming raw material gas into the processing chamber **1**, and a purge gas supply mechanism **16** configured to supply a purge gas into the processing chamber **1**. An example of the oxidant gas may include an ozone (O_3) gas. An example of a thin film to be formed may include a metal oxide film such as a zirconium oxide (ZrO_2) film. An example of the film-forming raw material gas used to form the ZrO_2 film may include tetrakisethylmethylamino zirconium (TEMAZ). An example of the purge gas may include an inert gas such as a nitrogen (N_2) gas.

The oxidant gas supply mechanism **14** includes an oxidant gas supply source **17**, an oxidant gas pipeline **18** through which the oxidant gas supplied from the oxidant gas supply source **17** flows into the processing chamber **1**, and an oxidant gas dispersion nozzle **19** formed of a quartz pipe. The oxidant gas dispersion nozzle **19** is connected to the oxidant gas pipeline **18**, and internally passes through a sidewall of the manifold **3**. Further, the oxidant gas dispersion nozzle **19** is bent upwardly, and extends vertically. A plurality of gas discharge holes **19***a* is formed at certain intervals in a longitudinal portion of the oxidant gas dispersion nozzle **19** such that the oxidant gas (for example, the O_3 gas) is uniformly discharged from each of the gas discharge holes **19***a* into the processing chamber **1** in a horizontal direction.

The film-forming raw material gas supply mechanism **15** includes a Zr source reservoir **20** that stores a liquid Zr source as a film-forming raw material therein, a Zr source pipeline **21** through which the liquid Zr source stored in the Zr source reservoir **20** flows, a vaporizer (VU) **22** coupled to the Zr source pipeline **21** and configured to vaporize the Zr source, a Zr source gas pipeline **23** through which a Zr source gas generated in the vaporizer **22** flows, and a Zr source gas dispersion nozzle **24**, which is formed of a quart pipe and connected to the Zr source gas pipeline **23**. The Zr source gas dispersion nozzle **24** passes through the sidewall of the manifold **3** internally, is bent upwardly, and is extended vertically. A carrier gas pipeline **22***a* through which a nitrogen (N_2) gas as a carrier gas flows, is connected to the vaporizer **22**. Here, two Zr source gas dispersion nozzles **24** are installed with the oxidant gas dispersion nozzle **19** interposed therebetween (see FIG. **2**). A plurality of gas discharge holes **24***a* is formed at certain intervals in a longitudinal portion of each of the Zr source gas dispersion nozzles **24** such that the Zr source gas is uniformly discharged from each of the gas discharge holes **24***a* into the processing chamber **1** in a horizontal direction. Only one of the Zr source gas dispersion nozzles **24** may be installed.

The purge gas supply mechanism **16** includes a purge gas supply source **25**, a purge gas pipeline **26** through which a purge gas supplied from the purge gas supply source **25** flows, and a purge gas nozzle **27** connected to the purge gas pipeline **26**. The purge gas nozzle **27** is installed to pass through the sidewall of the manifold **3**.

An opening/closing valve **18***a* and a flow rate controller **18***b* such as a mass flow controller are installed in the oxidant gas pipeline **18** such that the oxidant gas is supplied with its flow rate controlled. In addition, an opening/closing valve **26***a* and a flow rate controller **26***b* such as the mass flow controller are installed in the purge gas pipeline **26** such that the purge gas is supplied with its flow rate controlled.

A Zr source pressure-feed pipeline **20**a is installed to be inserted into the Zr source reservoir **20**. By supplying a pressure-feed gas such as a He gas through the Zr source gas pressure-feed pipeline **20**a, the liquid Zr source stored in the Zr source reservoir **20** is discharged to the Zr source pipeline **21**. A flow rate controller **21**a such as a liquid mass flow controller is installed in the Zr source pipeline **21**. An opening/closing valve **23**a is installed in the Zr source gas pipeline **23**.

An example of the Zr source may include an organic metal compound which is a liquid at room temperature, such as tetrakisethylmethylaminozirconium (TEMAZ). Another example of the Zr source may include tetrakisdiethyleaminozirconium (TDEAZ). In an alternative embodiment, the Zr source may be solid at room temperature. For the solid Zr source, a mechanism configured to vaporize the solid source and a mechanism configured to heat a related pipeline, and so on are required.

At a portion opposite to the oxidant gas dispersion nozzle **19** and the Zr source gas dispersion nozzles **24** in the processing chamber **1**, an exhaust vent **37** is formed to vacuum-exhaust the processing chamber **1**. The exhaust vent **37** has an elongated shape formed by vertically chipping a sidewall of the processing chamber **1**. At a portion corresponding outwardly to the exhaust vent **37** of the processing chamber **1**, a cover member **38** with a C-shaped section is installed by welding to cover the exhaust vent **37**. The cover member **38** extends upward along the sidewall of the processing chamber **1**, and defines a gas outlet **39** at the top of the processing chamber **1**. The processing chamber **1** is vacuumed through the gas outlet **39** by a vacuum-exhaust mechanism (not shown) including a vacuum pump. A tube-like heating unit **40**, which is configured to heat the processing chamber **1** and the wafers W accommodated therein, is installed to surround an outer circumference of the processing chamber **1**.

The respective units (or parts) of the film forming apparatus **100** are controlled by a controller **50** that is configured with a microprocessor such as a computer. For example, the controller **50** controls the supply/shutoff of each gas by operation of the opening/closing valves **18**a, **23**a and **26**a, the control of the flow rate of the gaseous or liquid source by the flow rate controllers **18**b, **21**a and **26**b, the control of the heating unit **40**, etc. The controller **50** is connected to a user interface **51**, which includes a keyboard or a touch panel display that enables an operator to input a command for managing the film forming apparatus **100**, and a display that visually displays an operation status of the film forming apparatus **100**.

Further, the controller **50** is connected to a storage unit **52**, which stores control programs executed by the controller **50** for various processes of the film forming apparatus **100** or programs (i.e., recipes) for executing processes of the respective units (or parts) of the film forming apparatus **100** according to a processing condition. The recipes are stored in a storage medium of the storage unit **52**. The storage medium may be a fixedly-installed medium such as a hard disk, or a portable medium such as a CDROM, a DVD, or a flash memory. Also, the recipes may be appropriately transferred from another device through a dedicated line.

Furthermore, depending on the case, the controller **50** reads an arbitrary recipe from the storage unit **52** and executes the read recipe according to a command that is inputted through the user interface **51**. In this way, a desired processing is performed using the film forming apparatus **100** under the control of the controller **50**.

(Film Forming Method)

Next, an example of the film forming method according to the second embodiment of the present disclosure will be described. In this embodiment, a film to be formed is an oxide film such as a metal oxide film. FIG. **3** is a timing chart showing an example of gas supply timings in the film forming method according to the second embodiment of the present disclosure. FIGS. **4**A to **4**D are views schematically showing a state of an object to be processed in major processes of this example.

First, as indicated by process (**1**) in FIG. **3**, a film-forming raw material gas is supplied into the processing chamber **1** in which objects to be processed (e.g., wafers) W are accommodated. In this example, the film-forming raw material gas is obtained by vaporizing TEMAZ. In this case, as shown in FIG. **4**A, metals M whose bonds are coupled with ligands L are adsorbed onto a surface of the wafer W. The film-forming raw material gas obtained by vaporizing TEMAZ contains an organic metal precursor. This allows the ligands L to be organic ligands L. Specifically, in this example, zirconium (Zr) is used as the metal M and the ligands L become the organic ligands L whose nitrogen (N) is bounded with a hydrocarbon group such as a methyl group (CH_3) or an ethyl group (CH_2CH_3).

Subsequently, as indicated by process (**2**) in FIG. **3**, the processing chamber **1** into which the film-forming raw material gas is supplied is exhausted, and subsequently, a purge gas is supplied into the processing chamber **1**. Thus, gas remaining in the processing chamber **1** is removed, and an internal atmosphere of the processing chamber **1** is converted from a film-forming raw material gas atmosphere to an inert purge gas atmosphere.

Thereafter, as indicated by process (**3**) in FIG. **3**, the oxidant gas is supplied into the processing chamber **1**. In this example, the supply process (**3**) of the oxidant gas includes a first supply process (**5**) of supplying the oxidant gas at a first concentration and a second supply process (**6**) of supplying the oxidant gas at a second concentration higher than the first concentration.

In the supply process (**3**), the first supply process (**5**) of supplying the oxidant gas at the first concentration (a relatively low concentration) is first performed. In this example, an ozone (O_3) gas is used as the oxidant gas. The first concentration of the O_3 gas in the first supply process (**5**) falls within a range of, e.g., 50 g/Nm^3 to 200 g/Nm^3. That is, the oxidant gas such as the O_3 gas, which falls within a range of 50 g to 200 g per 1 m^3, is supplied into the processing chamber **1**.

Subsequently, as shown in FIG. **4**B, the organic ligands L contained in the organic metal precursor are separated from the organic metal precursor. As a result, only the metals M contained in the organic metal precursor remains on the wafer W.

In this example, each of the organic ligands L contains hydrocarbon. In this case, the first supply process (**5**) may be performed under conditions where the hydrocarbon-containing organic ligands L are cut and an oxidation does not progress.

An example of the conditions applied in the first supply process (**5**) is as follows:

Concentration of O_3 gas: 50 to 200 g/Nm^3

Flow rate of (O_2+O_3) gas: 5 to 20 slm

Processing time: 30 sec to 2 min

Processing temperature: 200 to 300 degrees C.

Processing pressure: 66.5 to 266 Pa (0.5 to 2 Torr) wherein, 1 Pa is defined as 133 Torr. The flow rate of the (O_2+O_3) gas represents a sum of flow rates of the rest of the O_2 gas used in generating the O_3 gas and the generated O_3 gas.

Subsequently, process (**7**) is performed where the processing chamber **1** is exhausted and the organic ligands L separated from the organic metal precursor are removed from the interior of the processing chamber **1**. Thus, as shown in FIG. **4**C, the organic ligands L are removed from the processing chamber **1**. Then, a metal-hydroxy group (M-OH) or metal-oxygen-metal (M-O-M) (in this example, Zr—OH or Zr—O—Zr) is exposed and left on the wafer W in the processing chamber **1**.

The first supply process (**5**) is then followed by the second supply process (**6**). In this example, an oxidant gas used in the second supply process (**6**) is the same O_3 gas as that used in the first supply process (**5**). When the same oxidant gas is used in both the first and second supply processes (**5**) and (**6**), the oxidant gas used in the second supply process (**6**) may be obtained by concentrating the oxidant gas used in the first supply process (**5**) at a relatively high level. Thus, a concentrated O_3 gas is generated. A concentration (i.e., the second concentration) of the concentrated O_3 gas used in the second supply process (**6**) falls within a range of, e.g., 200 g/Nm^3 to 500 g/Nm^3. Specifically, the concentrated O_3 gas falling within a range of 200 g to 500 g per 1 m^3 is supplied into the processing chamber **1**.

Upon the supply of the concentrated O_3 gas into the processing chamber **1**, as shown in FIG. **4**D, the metal-hydroxy group (M-OH) or the metal-oxygen-metal (M-O-M) remaining on the wafer W is oxidized so that a metal oxide film containing metal oxides (MOx) is formed on the wafer W. In this example, a zirconium oxide (ZrO_2) film is formed as the metal oxide film.

In the second supply process (**6**), an oxidizing power of the oxidant gas (the concentrated O_3 gas in this example) may be strengthened to form the metal oxide film having a dense and good quality. To do this, the O_3 gas having increased concentration is used. An example of detailed conditions applied in the second supply process (**6**) is as follows:

Concentration of O_3 gas: 200 to 500 g/Nm^3
Flow rate of (O_2+O_3) gas: 10 to 20 slm
Processing time: 30 sec to 3 min
Processing temperature: 200 to 300 degrees C.
Processing pressure: 66.5 to 266 Pa (0.5 to 2 Torr)

The concentration of the concentrated O_3 gas in the second supply process (**6**) includes 200 g/Nm^3, which overlaps with the concentration (200 g/Nm^3) of the O_3 gas in the first supply process (**5**). However, if the concentration of the concentrated O_3 gas in the second supply process (**6**) is set to be 200 g/Nm^3, the concentration of the O_3 gas in the first supply process (**5**) may be set to be a value lower than 200 g/Nm^3. Similarly, if the concentration of the O_3 gas in the first supply process (**5**) is set to be 200 g/Nm^3, the concentration of the concentrated O_3 gas in the second supply process (**6**) may set to be a value more than 200 g/Nm^3.

Subsequently, as indicated by process (**4**) of FIG. **3**, the processing chamber **1** into which the oxidant gas is supplied is exhausted, and a purge gas is supplied into the processing chamber **1**. Thus, gas remaining in the processing chamber **1** is removed so that the internal atmosphere of the processing chamber **1** is converted from the film-forming raw material gas atmosphere to the inert purge gas atmosphere.

Thereafter, one cycle including a series of processes (**1**) to (**4**) is repeated several times until the metal oxide film has a predetermined film thickness. Thus, the metal oxide film (the ZrO_2 film in this example) is formed on the wafer W.

(Metal Oxide Film)

FIG. **5**A is a sectional view showing a metal oxide film formed by a film forming method according to a comparative example, and FIG. **5**B is a sectional view showing a metal oxide film formed by the film forming method according to the second embodiment of the present disclosure.

In this comparative example, an organic metal precursor is used as the precursor and a concentration of the O_3 gas is increased to strengthen an oxidizing power thereof. Under this condition, oxidization of the organic metal precursor adsorbed onto the wafer W causes, as shown in FIG. **5**A, a thickness of a formed metal oxide film **50** to become thick in a periphery E of the wafer W and thin in a central portion C thereof. The reason for this is that, when the organic metal precursor is used as the precursor, ligands L become organic ligands such as CH_3 or C_2H_5, but the O_3 gas having the increased concentration causes a strong oxidizing power, thus oxidizing the organic ligands L. As described above, the oxidization of the organic ligands L generates a H_2O gas or a CO_x gas. When nitrogen is contained in the organic metal precursor, a NO_x gas is additionally generated.

Specifically, the H_2O gas inactivates the O_3 gas. This creates a situation where the O_3 gas hardly reaches the central portion C of the wafer W, thus making it difficult to oxidize the central portion C of the wafer W. As a result, the metal oxide film **50** is formed to have a thick thickness in the periphery E of the wafer W and a thin thickness in the central portion C thereof.

In addition, the O_3 gas is consumed in the course of both the oxidation of the metal and the oxidation of the organic ligands L, which deteriorates the actual oxidizing power even weaker than a designed oxidizing power. This makes it difficult to form the metal oxide film **50** having a dense and good high quality.

According to the above embodiment of the present disclosure, in the first supply process (**5**), the O_3 gas having a relatively low concentration is used to separate the organic ligands L from the organic metal precursor. In addition, the first supply process (**5**) is performed under conditions where the separated organic ligands L are not oxidized. Thereafter, the organic ligands L are exhausted from the processing chamber **1** (in process (**7**)). Subsequently, in the second supply process (**6**), the concentrated O_3 gas having a relatively high concentration is used to separate the organic ligands L from the organic metal precursor. Thus, the metal-hydroxy group (M-OH) or the metal-oxygen-metal (M-O-M) which is exposed on the wafer W, is oxidized.

As described above, according to the above embodiment, since the organic ligands L are separated in the first supply process (**5**), although the concentrated O_3 gas having relatively high concentration is used in the second supply process (**6**), it is possible to prevent, e.g., the H_2O gas from being generated, thereby preventing the O_3 gas from being inactivated.

Therefore, according to this embodiment as shown in FIG. **5**B, the metal oxide film **50** is uniformly formed on the wafer W over all areas including the periphery E and the central portion C of the wafer W. As a result, even if the concentration of the oxidant gas used in oxidizing the metal is increased to strengthen the oxidizing power thereof, it is possible to form the metal oxide film **50** with good in-plane uniformity.

In addition, in the second supply process (**6**), since the metal-hydroxy group (M-OH) or the metal-oxygen-metal (M-O-M) is oxidized under a state where almost none of the organic ligands L exist, hardly none of the concentrated O_3 gas is consumed for the oxidation of the organic ligands L. Therefore, the actual oxidizing power becomes very close to the designed oxidizing power. This makes it possible to form the metal oxide film **50** with a dense and good film quality as compared to that in the comparative example.

(Oxidant Gas Supply Source)

Next, an example of the oxidant gas supply source **17** which is provided to perform the film forming method according to the second embodiment of the present disclosure will be described.

FIG. **6** is a block diagram showing an example of a configuration of the oxidant gas supply source **17** which is provided to perform the film forming method according to the second embodiment of the present disclosure.

As shown in FIG. **6**, the oxidant gas supply source **17** includes an oxidant gas generating unit configured to generate the oxidant gas (e.g., the O_3 gas), and an oxidant gas booster configured to concentrate the oxidant gas generated in the oxidant gas generating unit and generate a concentrated oxidant gas. In this example, an ozonizer **171** is used as the oxidant gas generating unit and an ozone booster **172** is used as the oxidant gas booster.

The ozonizer **171** generates the O_3 gas using a silent discharge. The generated O_3 gas is sent to the ozone booster **172** through a valve V**1**.

The ozone booster **172** includes a first path through which the O_3 gas generated in the ozonizer **171** directly flows to the flow rate controller **18***b*, a second path in which a nitrogen oxide (NO_x) contained in the O_3 gas is removed by a NO_x removing unit **173**, and a third path through which the concentrated O_3 gas flows to the flow rate controller **18***b*.

The first path through which the O_3 gas generated in the ozonizer **171** directly flows to the flow rate controller **18***b* is used in the first supply process (**5**). Specifically, in the first supply process (**5**), the O_3 gas generated in the ozonizer **171** is supplied into the processing chamber **1** through the flow rate controller **18***b*. The valve V**1** is installed between the ozonizer **171** and the ozone booster **172**. A valve V**2** is used to guide the O_3 gas flowing through the valve V**1** to the NO_x removing unit **173**. A valve V**4** is used to guide the O_3 gas to the third path (as a concentration path) in which the O_3 gas is subjected to a concentration process. Valves V**5** to V**8** are arranged in the concentration path. A bypass valve V**9** is used to allow the concentrated O_3 gas to bypass the ozone booster **172**. When the valves V**4** to V**9** are closed and the valves V**1** and V**2** are opened, the O_3 gas generated in the ozonizer **171** is sent to the NO_x removing unit **173**. The NO_x removing unit **173** is configured to remove the nitrogen oxide (NO_x) contained in the O_3 gas that is generated by the silent discharge. The nitrogen oxide-free O_3 gas is sent to the flow rate controller **18***b* through a valve V**3**.

The third path is used in the second supply process (**6**) to generate the concentrated O_3 gas. Specifically, the second supply process (**6**) includes concentrating the O_3 gas generated in the ozonizer **171** using a concentrating unit **174** of the ozone booster **172** and supplying the concentrated O_3 gas into the processing chamber **1** via the flow rate controller **18***b*. When the valve V**3** is closed and the valve V**4** is opened, the O_3 gas is guided to the concentrating unit **174** where it is subjected to the concentration process. Thus, the concentrated O_3 gas is supplied to the flow rate controller **18***b*. As described above, the valves V**5** to V**8** are installed in the concentration path. The valve V**5** is used to discharge the concentrated O_3 gas obtained by the concentrating unit **174** therethrough. The valve V**6** is used to guide the concentrated O_3 gas to a buffer tank **175**. The valve V**7** is used to discharge the concentrated O_3 gas stored in the buffer tank **175** toward the flow rate controller **18***b*. The valve V**8** is used to bypass the buffer tank **175**. When the valve V**8** is closed and the valves V**4** to V**7** are opened, the nitrogen oxide-free O_3 gas obtained at the NO_x removing unit **173** flows to the concentrating unit **174**. In the concentrating unit **174**, the nitrogen oxide-free O_3 gas is concentrated. The concentrated O_3 gas is sent to the buffer tank **175**. The concentrated O_3 gas charged in the buffer tank **175** is sent to the flow rate controller **18***b* by opening the valve V**7**.

In some embodiments, the concentration process of the O_3 gas may be performed in the course of forming the metal oxide film **50** without involving the second supply process (**6**). With this configuration, it is possible to generate the concentrated O_3 gas during the formation of the metal oxide film **50** without involving the second supply process (**6**), and charge the concentrated O_3 gas in the buffer tank **175** (indicated by "charge" in FIG. **3**). In the second supply process (**6**), the concentrated O_3 gas charged in the buffer tank **175** is discharged to the processing chamber **1** while maintaining the charge of the buffer tank **175** at a constant level. This makes it possible to prevent the concentrated O_3 gas from being insufficient during the formation of the metal oxide film **50**.

The bypass valve V**8** is used to exhaust or purge the concentration path through which the concentrated O_3 gas generated in the concentrating unit **174** flows. By opening the bypass valve V**8** and closing the valves V**6** and V**7**, the concentrated O_3 gas generated in the concentrating unit **174** can be directly sent to the flow rate controller **18***b*. Similarly, the bypass valve V**9** is used to exhaust or purge the first path through which the O_3 gas generated in the ozonizer **171** is flows.

As described above, the oxidant gas supply source **17** including the ozone booster **172** configured as above can be used to perform the film forming method according to the second embodiment of the present disclosure.

Although the present disclosure has been described according to some embodiments, the present disclosure is not limited thereto. A variety of modifications may be made without departing from the spirit of the disclosures. The above embodiment is not unique for embodiments of the present disclosure.

While in the above embodiments the material being liquid at room temperature has been described to be used as the source, in some embodiments the material may be solid. In addition, while in the above embodiments, the substrate processing apparatus has been described with the batch-type vertical substrate processing apparatus, the present disclosure is not limited to thereto.

Furthermore, while in the above embodiments, the specific process conditions has been described to be applied in the first supply process (**5**) and the second supply process (**6**), the process conditions may be changed in various ways. In some embodiments, an oxide film can be formed by setting the supply process (**3**) of supplying the oxidant gas into the processing chamber **1** to include the first supply process (**5**) of supplying the oxidant gas at the first concentration and the second supply process (**6**) of supplying the oxidant gas at the second concentration higher than the first concentration.

Furthermore, while in the above embodiments, as indicated by process (**2**) in FIG. **3**, the gas remaining in the processing chamber **1** has been described to be removed by exhausting the processing chamber **1** into which the film-forming raw material gas is supplied, followed by supplying the purge gas into the processing chamber **1**, the present disclosure is not limited thereto. In an alternative embodiment, only one of the exhaustion of the processing chamber **1** and the supply of the purge gas into the processing chamber **1** may be performed.

Similarly, in process (**4**), only one of the exhaustion of the processing chamber **1** and the supply of the purge gas into the processing chamber **1** may be performed.

According to the present disclosure in some embodiments, it is possible to provide a method and apparatus which is capable of forming a metal oxide film having a dense and good in-plane uniformity even when a concentration of an oxidant gas used to oxidize metal is increased to strengthen an oxidizing power thereof.

While certain embodiments have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the disclosures. Indeed, the novel methods and apparatuses described herein may be embodied in a variety of other forms. Furthermore, various omissions, substitutions and changes in the form of the embodiments described herein may be made without departing from the spirit of the disclosures. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the disclosures.

What is claimed is:

1. A method of forming a metal oxide film on an object to be processed by repeatedly performing a cycle comprising:

supplying a film-forming raw material gas including an organic metal precursor into a processing chamber for the organic metal precursor to be adsorbed onto the object to be processed;

performing at least one of exhausting the processing chamber and supplying a purge gas into the processing chamber to remove gas remaining in the processing chamber;

supplying a first oxidant gas into the processing chamber at a first concentration of the first oxidant gas to separate organic ligands contained in the organic metal precursor from the organic metal precursor while leaving metals contained in the organic metal precursor on the object to be processed under conditions where the separated organic ligands are not oxidized;

exhausting the processing chamber to remove the organic ligands, which are separated from the organic metal precursor, from the processing chamber;

supplying a second oxidant gas into the processing chamber at a second concentration of the second oxidant gas higher than the first concentration of the first oxidant gas to oxidize the metals left on the object to be processed under a state where almost none of the organic ligands exist; and

performing at least one of exhausting the processing chamber and supplying the purge gas into the processing chamber to remove gas remaining in the processing chamber.

2. The method of claim **1**, wherein the organic ligands contain hydrocarbon.

3. The method of claim **1**, wherein the first concentration of the first oxidant gas falls within a range of 50 g/Nm^3 to 200 g/Nm^3,

wherein the second concentration of the second oxidant gas falls within a range of 200 g/Nm^3 to 500 g/Nm^3.

4. The method of claim **1**, wherein a series of supplying a film-forming raw material gas to performing at least one of exhausting the processing chamber and supplying the purge gas are performed several times.

5. The method of claim **1**, wherein each of the first and second oxidant gas is an ozone gas.

6. The method of claim **1**, wherein supplying a first oxidant gas is performed by supplying the first oxidant gas generated by an oxidant gas generating unit into the processing chamber, and

wherein supplying a second oxidant gas is performed by concentrating the first oxidant gas generated by the oxidant gas generating unit and supplying a concentrated first oxidant gas as the second oxidant gas into the processing chamber.

7. The method of claim **6**, wherein the first oxidant gas is concentrated in the course of forming the oxide film without involving supplying a second oxidant gas, and

wherein the concentrated first oxidant gas is generated in the course of forming the oxide film without involving supplying a second oxidant gas.

8. The method of claim **7**, wherein the concentrated first oxidant gas is charged in a buffer tank, and

wherein supplying a second oxidant gas is performed by supplying the concentrated first oxidant gas charged in the buffer tank into the processing chamber.

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